

## Description

## Maraging steel golf club head

The invention concerns a golf club head that is at least partly made of a corrosion-resistant, precipitation-hardened maraging steel.

Such a golf club head is known e.g. from the published US patent application 20020045490. At least the strike surface of the golf club head illustrated there, which has a hollow construction, is made of a precipitation-hardened, corrosion-resistant maraging steel with a martensite temperature  $M_s > 130^\circ\text{C}$ . The maraging steel described there has a chromium content of 10.0 to 11.5 wt.%, a molybdenum content of 1.5 to 2.5 wt.% and nickel content of 8.5 to 10.5 wt.%, the rest being iron. This maraging steel is precipitation-hardened by a titanium content of 1.2 to 1.6 wt.% of titanium. An alloy of vanadium serves as a carbide- and/or nitride catcher. With this maraging steel, a tensile strength of more than 1700 MPa can be achieved.

However it has proved to be desirable to form at least the strike surface of golf club heads such that much higher tensile strengths can be achieved, i.e. tensile strength  $R_m > 2000\text{ Mpa}$ , while at the same time achieving a very high degree of hardness. This is either impossible or only conditionally possible using the maraging steel mentioned in the beginning.

In addition to the maraging steels known from the US patent application 20020045490 mentioned in the beginning, alloys that are fully martensitic in the solution-annealed state are known that are age-hardenable by heat treatment. But usually these maraging steels are used as spring steels. While manufacturing spring steels, particular importance is attached to its isotropic deformability, which plays an insignificant role in its use as the basic material for golf club heads. Spring steels of this type are known e.g. from the WO 01/53556A1, which comes from the same applicant. Furthermore, spring

steels are processed in the solution-annealed state and/or are weakly cold-formed and age-hardened.

Surprisingly, it has been seen that the maraging steels described there are not only suitable for use as spring steels but also as the basic material for golf club heads if an additional cold-forming takes place before age-hardening.

By modifying the maraging steels described in the WO 01/53556A1 that are optimized for use as spring steels by the manufacturing processes described there, the present invention can be used to manufacture maraging steels that are characterized by extremely high Vickers hardnesses, tensile strengths, yield strengths, very high alternating flexure strengths, storable energies and/or reciprocal damping. In the present invention, not much importance is attached to the isotropic deformability that is in the foreground in the case of WO 01/53556A1.

Therefore the task of the present invention is to make available new maraging steels for golf club heads particularly for the strike surfaces of golf club heads that clearly surpass the maraging steels used to date in relation to the Vickers hardnesses, tensile strengths and yield strengths.

Moreover, it is the task of the present invention to specify a maraging steel that is characterized by high alternating flexure strengths, storable energies and reciprocal damping.

In accordance with the invention the task is solved by a golf club head that is at least partly made of a corrosion-resistant, precipitation-hardened maraging steel with a martensite temperature  $M_s \geq 130^\circ\text{C}$ , a ferrite content  $^{\circ}\text{Ferrite} < 3\%$ , wherein the maraging steel essentially consists of 6.0 to 9.0 wt.% nickel, 11.0 to 15.0 wt.% chromium, 0.1 to 0.3 wt.% titanium, 0.2 to 0.3 wt.% beryllium, the rest being iron together with unavoidable impurities resulting from production. The maraging steel in accordance with the invention exhibits a tensile strength  $R_m > 2000\text{ MPa}$  and a yield strength  $R_{p0.2} > 1900\text{ MPa}$ .

For the purpose of illustration of this maraging steel in accordance with the invention figure 1 shows a so-called Schaeffler diagram illustrating the assortment of alloys in accordance with the invention. This figure matches figure 6 from the WO 01/53556 mentioned in the beginning.

Typically up to 35% of the chromium content can be replaced by molybdenum and/or tungsten.

In an advanced embodiment of the present invention the maraging steel can contain up to 4 wt.% of copper, which further enhances the corrosion-resistance. Apart from that, up to 50% of the nickel content can be replaced by cobalt, which is more expensive in comparison with nickel. This replacement can be carried out without adversely affecting the physical and technical properties of the alloy.

The maraging steel can comprise at least one of the elements manganese, silicon, aluminum, or niobium in individual proportions of less than 0.5 wt.%.

To achieve a qualitatively high quality maraging steel, the maraging steel in accordance with the invention comprises contents of carbon, nitrogen, sulfur, phosphorous, boron, hydrogen or oxygen in individual proportion that is adjusted to less than 0.1 wt.%. If these proportions are exceeded, undesired carbide, boride, or nitride precipitates result, which have a negative effect on the technical properties of the material.

In a preferred embodiment, the maraging steel in accordance with the invention comprises up to 0.1 wt.% cerium or cerium misch metal as a deoxidizing agent.

To correctly adjust the components for the alloy melt, it has been found that the martensite temperature  $M_s$ , which must be above 130 °C according to the present invention, can be adjusted by equation (1):

$$M_s = [629.45 - 6.8(\text{Cr} + 1.2 \text{ Mo} + 0.6 \text{ W}) - 24.5(\text{Ni} + 0.15 \text{ Co}) - 13.2 \text{ Mn} - 11.2 \text{ Si} - 670(\text{C} + \text{N})] \text{ } ^\circ\text{C}. \quad (1)$$

The proportion of ferrite can be adjusted in percent by weight according to equation (2):

$$^\circ\text{Ferrite} = [11.8 \text{ Si} + 7.92(\text{Cr} + \text{Mo} + 0.5 \text{ W}) + 15.84 \text{ Ti} - 2.91 \text{ Mn} - 5.83(\text{Ni} + 0.3 \text{ Co}) - 174.9(\text{C} + \text{N}) - 77.08] \text{ wt. } \% \quad (2)$$

According to the invention, the ferrite content must not exceed 3%; otherwise brittle theta phases or great losses in Vickers hardness may result. The two equations restrict the martensite field in the Schaeffler diagram.

The present alloys are typically produced by casting a melt in a crucible or oven under vacuum or under a protective gas atmosphere. The melt temperatures are approximately 1500 °C.

The melt is then poured into a mold. The ingots from the present alloys are then bloomed at a temperature of approximately 1000 °C to 1200 °C and are then hot formed into a strip at  $100 \text{ } ^\circ\text{C} \leq T_1 \leq 1150 \text{ } ^\circ\text{C}$ . Low heat rolling temperatures are chosen to minimize the edge zones depleted of free beryllium.

Then a solution annealing (homogenization) of the strip takes place at  $850\text{ }^{\circ}\text{C} \leq T_2 \leq 1100\text{ }^{\circ}\text{C}$ ., depending on the choice of annealing time.

After cooling the strip to a temperature  $T_3 \leq 300\text{ }^{\circ}\text{C}$ , the strip is ground at a temperature corresponding approximately to room temperature, the intent being to completely remove the edge zone depleted of free beryllium.

Then the strip is cold formed to a cold forming degree that is greater or equal to 60%, particularly forged, extruded or rolled.

Subsequently the strip is subjected to a heat treatment at  $400\text{ }^{\circ}\text{C} \leq T_4 \leq 550\text{ }^{\circ}\text{C}$ . The heat treatment is carried out for 1 to 10 hours. By this heat treatment the maraging steels in accordance with the invention exhibit tensile strengths  $R_m > 2400\text{ MPa}$ . With a cold forming degree of less than 60%, tensile strengths  $2000 < R_m < 2400\text{ MPa}$  are achieved.

In an advanced embodiment of the present invention, this heat treatment is followed by another heat treatment at  $350\text{ }^{\circ}\text{C} \leq T_5 \leq 470\text{ }^{\circ}\text{C}$ . This heat treatment is carried out for 10 to 100 hours. Due to this additional special heat treatment it is possible to obtain particularly high tensile strengths  $R_m$  of approximately 2800 MPa.

All in all, the present invention makes available the basic materials for golf club heads and particularly for their strike surfaces that besides the enormous tensile strengths also exhibit Vickers hardnesses  $HV > 700$  or  $>800$  in special cases.

Furthermore, yield strengths  $R_{p0.2} > 2100$  MPa can be obtained at the same time. In the case of the special second heat treatment yield strengths  $R_{p0.2} > 2600$  MPa can be achieved.

Typically, the maraging steels in accordance with the invention are characterized by alternating flexure strengths  $\sigma_{bw}$  (in typical  $10^3$  load changes) of about 1350 MPa and/or in particular cases of 1550 MPa in the absence of inner and outer notches.

In addition, the maraging steels in accordance with the invention exhibit, due to the high strengths, an extremely high storable energy  $R_m^2 / E$ -module of approximately 30 MPa and in special cases of 40 MPa, which is particularly advantageous for use as strike surface. Moreover, the basic materials in turn exhibit very low damping values, which is attributed to the high strengths and the very fine martensitic structure in which the grains lie in the range of approximately 1  $\mu\text{m}$ .

The basic materials in accordance with the invention can be soft- or hard-soldered or even welded. Its ability to be welded is particularly advantageous because then the strike surfaces made of the alloys in accordance with the invention can be combined with the golf club heads firmly and permanently. The strike surfaces can be welded with almost all other basic materials known in relation to golf clubs e.g. other corrosion-resistant steels.